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# Precision Studies of Gas-Surface Collisional Energy Transfer at Complex Interfaces

**Final Technical Report: FA9550-06-1-0139**

**February 1, 2006 – November 30, 2009**

**PI: Professor Steven J. Sibener, The University of Chicago**

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### **Abstract**

In this Final Technical Report we describe the accomplishments that have occurred in this AFOSR funded project. It has been a very productive period: we have studied the dynamical properties of polymeric interfaces in nanoconfinement; demonstrated the efficacy of using hyperthermal neutral atomic beams for sputtering; developed refined models of hyperthermal gas-surface energy/momentum exchange; developed a new method for probing molecular diffusion through polymeric thin films; and explored the oxidative chemistry of gold and the chemistry/photochemistry of NO/NiO interfaces. As part of this program we implemented a new *in situ* FTIR spectrometer system that is coupled with a molecular beam instrument for real-time studies of interfacial sticking and chemistry, as well as a high-intensity/laser-ignition pulsed molecular beam for producing hyperthermal beams of neutrals. This hyperthermal source has been used for studies of collisional energy transfer and in exploratory experiments on sputtering due to neutral atom bombardment. This was accomplished during a period of great disruption: our laboratories were relocated from their former location, the Research Institutes Bldg, to the new Gordon Center at the U. of Chicago. All instruments are now fully operational.

## **I. Introduction**

The scattering of atomic and molecular beams from well-characterized surfaces is an incisive method for studying the dynamics of gas-surface interactions. Such experiments provide molecular-level mechanistic details of energy and momentum exchange at interfaces, as well as fundamental understanding of the various chemical processes responsible for heterogeneous reactivity. They also serve as precision tools for examining the properties of clean, alloyed, adsorbate decorated, and thin-film covered interfaces. In essence, depending on one's interest, the focus can be on the actual scattering dynamics and the information so obtained on collisional energy transfer, or on how the observed elastic and inelastic scattering distributions can be used to ascertain static and dynamical information on the properties of the interface itself.

Our approach utilized three arguably unique UHV gas-surface scattering instruments for probing energy exchange, reaction, and penetration at interfaces as well as *in situ* FTIR and XPS spectroscopy. This research program has led to improved understanding of physical and chemical thin film properties on the nanoscale, collisional energy exchange at complex interfaces, gaseous condensation, and chemical transport through polymeric and molecular thin film systems.

## **II. Relevance to AFOSR/DoD Interests**

This program has dealt with delineating the fundamental atomic-level mechanisms which govern gas-surface collisional energy transfer over an extraordinarily large range of collision energies, spanning milli-eV to multiple-eV encounters. The systems emphasized were thin films of polymers, self-assembling overlayers, molecule-decorated interfaces, and interfaces having aligned features. The studies significantly extended the class of gas-surface collision systems for which energy exchange processes can be verifiably and quantitatively modelled. Such fundamental understanding is needed for the development of advanced flight surfaces and propulsion systems. It is also important for developing a more accurate understanding of momentum accommodation and hence aerodynamic drag in hypervelocity environments, important for high-performance aircraft behavior and orbital decay in low-Earth-orbit. The experiments explored the utility of atomic-beam scattering for probing such questions for chemically complex and technologically relevant organic coatings, bringing a truly surface-sensitive and non-destructive scattering probe to the utility level of more traditional x-ray and

neutron scattering methods. Other work on embedding/transport/releasing molecules into/from SAM and polymeric films, including multilayer barrier films, are also of interest due to the central role such events play in materials passivation, packaging, and chemical protection. The work on sticking and condensation under non-equilibrium conditions is important for refining our understanding of such phenomena.

### **III. Personnel: Current and Past Group Members**

Our AFOSR research program has been quite successful in attracting and educating some of the best young scientific talent in the country, including undergraduates, graduate students, and postdoctoral fellows. We also wish to emphasize that we have been quite successful in attracting women and minorities to our program. During the past year 7 of our group members were women, including one under-represented minority. The PI recognizes that the vitality of American science will depend on the involvement of such individuals at all levels of training.

#### **Current Personnel** (PD: Postdoc; GS: Grad Student; UG: Undergrad; HS: High School):

Steven J. Sibener, Carl William Eisendrath Professor and PI; Dr. Kevin Gibson (Research Scientist); Dr. Daniel Killelea (PD), Dr. Chris Fleming (PD), Lieve Teugels (GS), Miki Nakayama (GS), Hanqiu Yuan (GS), Jim Becker (GS), Gaby Avila-Bront (GS), Ryan Brown (GS), Tuo Wang (GS), Qian Qian Tong (GS), Stephanie Fronk (UG), Paul Kim (UG), William Letsou (UG), Cati Crawford (HS), Jessica Durden (HS), Paul Bissonnette (HS), Karen Liu (HS).

#### **Recent Sibener Group Alumni Who Contributed to AFOSR Projects During the Past**

##### **Grant Period (PD: postdoc; GS: graduate student; UG: undergraduate):**

Nataliya Yufa (GS, postdoc at the University of Cambridge), Miriam Freedman (GS, postdoc at CIRES, Boulder, CO); Amadou Cisse (GS); Ken Nicholson (PD, Cabot Microelectronics/Northeastern Illinois University); Aaron Rosenbaum (GS, Intel); Bill Isa (GS, Intel); Seth Darling (GS, Center for Nanoscale Materials – Argonne National Lab); Ben Zion (GS, E-Ink/Research staff at Penn State); Scott Kelber (UG, now at CalTech); Sarah Jones (UG, now at Harvard); Patrick Sullivan (UG, first at Stanford and now at NREL).

##### **Doctoral Dissertations with Primary Support from this Grant:**

Amadou L. Cisse, *Photodegradation of Poly(methyl methacrylate) and Applications in Surface Science and Diffusion Studies*, December, 2007

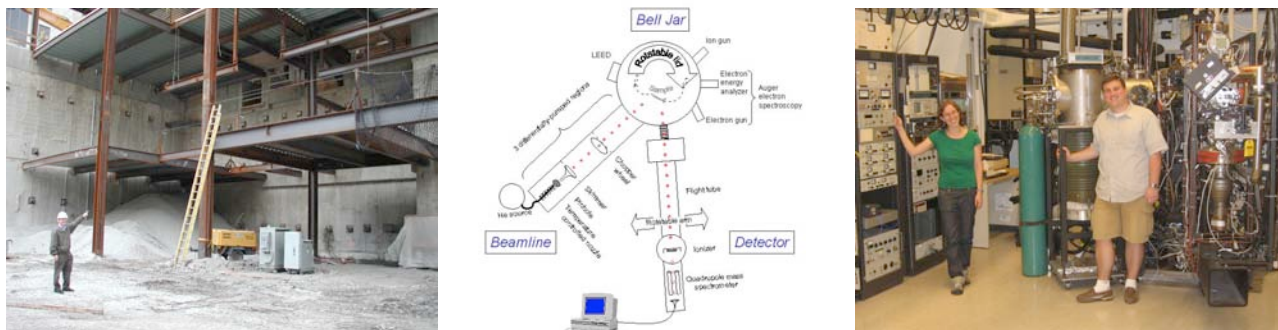
Miriam A. Freedman, *Interfacial Dynamics of Self-Assembled and Confined Complex Organic Materials*, March 2008.

## IV. Facilities

The key facilities during the past grant period were our 3 arguably unique gas-surface scattering instruments complemented by UHV-STM. These are briefly summarized as follows: The first scattering instrument has been constructed for high resolution (momentum and energy) studies, and is capable of single-phonon, few-phonon, and multiphonon interactions. The second is a recently upgraded beam-surface scattering and photochemistry instrument that now includes *in situ* FTIR spectroscopy. The third of these is a unique three-supersonic-beam UHV instrument which can carry out studies of interfacial energy transfer spanning ultra-cold thru hyperthermal energies. The last current facility is a UHV-SPM, giving us the ability to study the structure of molecular overlayers from their crystalline state until desorption/decomposition occurs. Taken together, these facilities give us arguably unique capabilities in the world for executing precision studies of complex interfaces with definitive structural characterization. The following paragraphs briefly describe these instruments.

### IV.1. High Energy- and Momentum- Resolution Scattering Facility

The high energy/momentum resolution neutral particle scattering instrument is shown in **Figure 1**. (Also shown the new Gordon Center under construction; all labs are now up and running in their new home.) The supersonic nozzle beam source is cryogenically cooled with a closed-cycle He refrigerator, giving the capability to "dial" a given nozzle temperature between  $\sim 40 - 300\text{K}$  (corresponding to wavevectors from  $1.56\text{-}0.57 \text{ \AA}^{-1}$ ). The beamline generates intense cw He beams ( $I \sim 2 \times 10^{19} \text{ atoms/sr/sec}$ ) of extremely narrow velocity dispersion ( $\Delta v/v \sim 0.75\%$ ,



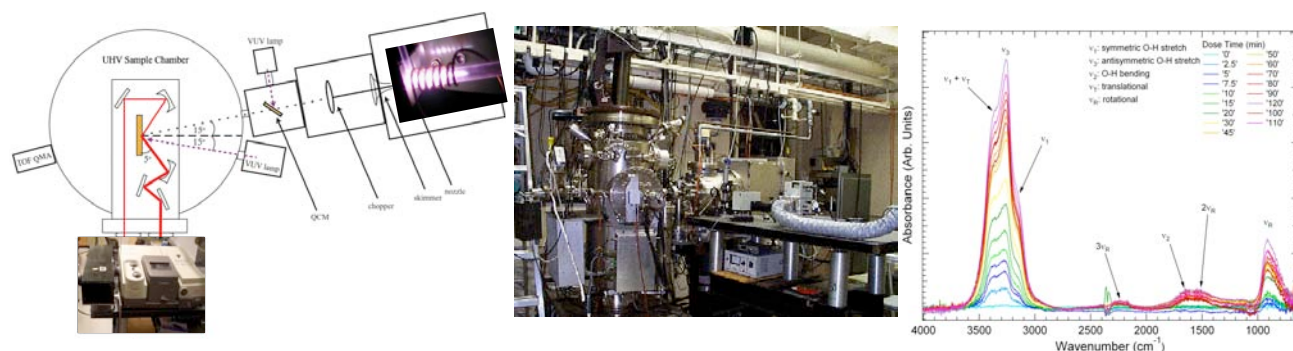
**Figure 1. The PI pointing at his new labs under construction. Schematic (top view) and photo of the high energy- and momentum resolution He atom scattering facility in its new home in the Gordon Center at UChicago.**

speed ratios of over 220) and can be connected in 3 positions, giving wide variability of incident geometry. These beams are then chopped into short pulses or a pseudo-random pulse sequence. The crystal chamber has a base pressure in the  $10^{-11}$  torr range, and contains LEED, Auger, XPS,

sputtering, and RGA capabilities. The target mount has all necessary degrees of freedom, and can be cooled or heated. Finally, the detector (right side of the photo) is a massive, 2-ton assembly which rotates ca.  $\pm 22^\circ$  under computer control with  $0.2^\circ$  resolution and flightpath 100.5 cm. Its mass 4 background of 1-10 Hz corresponds to a He partial pressure of  $10^{-14}$  torr.

#### **IV.2. Combined Molecular Beam/Fourier Transform Spectroscopy Facility:**

The molecular beam/FTIR experiments were conducted in a two-level UHV system, **Figure 2**, with base pressure  $4 \times 10^{-11}$  torr. The upper level of the chamber is equipped with a double-pass CMA Auger system, low energy electron diffraction (LEED), an XPS source,

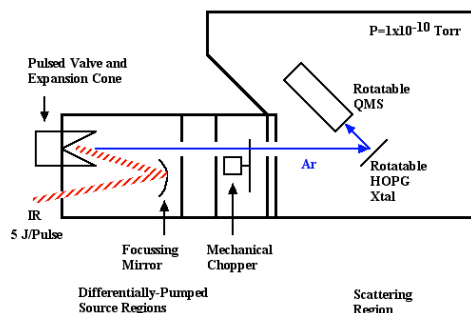


**Figure 2. Left: Beam/Photochemistry/FTIR Apparatus. Center: Photo. Right: Real-time FTIR Spectra of Water Film Growth Using Supersonic Beam Deposition.**

and a sputter gun. The lower level contains a new (2008) high-throughput FTIR optics train to monitor on-surface chemical moieties, a 3-fold differentially pumped supersonic beam source, and a mass analyzer to characterize the beam. The geometry is arranged so that the focus of the FTIR spot is coincident with the molecular beam on the crystal surface. Sample temperatures can span the range from 120K to >1000K. This lab has played a major role in the work on embedding molecular species into SAMs, as well as diffusion through polymeric thin films.

#### **IV.3. Three-Supersonic-Beam Gas-Surface Scattering Facility:**

The third scattering apparatus, **Figure 3**, consists of three supersonic molecular beam sources, a UHV chamber with rotatable quadrupole mass spectrometer, and the controlling computer system. The molecular beam source chamber contains three quadruply differentially pumped molecular beams horizontally co-planar and aligned and collimated to a single scattering center in the UHV chamber. Each beam has a computer-controlled beam shutter which can be used for slow modulation experiments or computer-tailored sequential dosing experiments; the center beam also has a 10 to 400 Hz chopper (conventional or cross-correlation) that resides 21.21 cm from the scattering center. The UHV chamber contains the crystal mount with full



**Figure 3. Schematic view (left) and photo (right) of the hyperthermal scattering facility. This instrument has been used for many of the hyperthermal embedding and sputtering experiments.**

It also contains an independently rotatable and doubly-differentially pumped quadrupole mass spectrometer with electron bombardment ionizer 14.45 cm from the scattering center. There is also a post-collision chopper for time-of-flight measurements *without concern for residence time limitations* that are associated with pre-collision modulation.

## **V. Research Overview**

The past grant period has been scientifically quite productive, as indicated by the ten publications that have come from this effort. These activities have encompassed the surface dynamics of polymers under nanoscale confinement (3 manuscripts), a new method of determining molecular diffusion through polymer thin films (1 manuscript), hyperthermal scattering from graphite to refine our understanding of collisional energy transfer in this important regime (1 manuscript), oxidative surface chemistry of gold and photochemistry of NO on NiO (3 manuscripts), and our first work on neutral sputtering induced by hyperthermal neutrals (2 manuscripts). Moreover, we have begun to explore issues of sticking and gaseous condensation under non-equilibrium flow conditions.

During the past grant period we have also built several new capabilities into our beam laboratories, and have learned how they can be optimally used. Most notable among these are the new combined Fourier Transform Infrared/Beam-Surface Interactions Instrument which allows us to take IR spectra in real-time during surface sticking/condensation/reactive chemistry experiments. The optically bright glancing-angle optics that we spent much time and money developing are now fully operational. Moreover, we also constructed a hyperthermal neutral atom beam source, modelled directly on (and with the much appreciated assistance of) Prof. Tim Minton at Montana State. This source allows us to carry out neutral scattering experiments of energetic rare gases in the formally difficult neutral beam energy regime of 5 through greater

than 50 eV. It also provides a wonderful method of producing reactive species such as ground state  $O(^3P)$  atoms, again with unusually high kinetic energies. Finally, we have developed an excellent UHV-STM and procured (in conjunction with our NSF-MRSEC Center) a commercial Asylum AFM for imaging under ambient environment conditions. Data taken with these SPM instruments emphasized to us the importance of knowing, precisely, what is occurring locally on the surfaces we study in our scattering labs. Accordingly, we wrote a DURIP Instrumentation Proposal for FY2009 to upgrade our STM to be a true variable-temperature (cryogenic plus elevated temperature operation) combined STM/AFM instrument; this proposal was selected for funding during FY 2009.

## **VI. AFOSR Sponsored Accomplishments and Publications During the Past Grant Period**

Below please find a summary of our publications from the last grant period:

*Hyperthermal Neutral Ar Atom Sputtering of Multilayer Thin Films of p-Xylene Adsorbed on Rh(111)*, K. D. Gibson and S. J. Sibener, *J. Phys. Chem. C*, Article ASAP, DOI:

10.1021/jp906239z (4 pages) (Web Published Dec. 7, 2009).

Hyperthermal neutral Ar atoms ( $\langle E \rangle = 12$  eV) were used to sputter molecules from thin films of *p*-xylene adsorbed on Rh(111). This was done for several different film thicknesses, and the energy and intensity of the sputtered *p*-xylene was measured as a function of both the incident angle of the Ar and the ejection angle of the sputtered *p*-xylene. The first layer is not sputtered. For thicker films, up to a coverage equivalent to 16 layers, molecules are ejected from the surface with a yield of at most 0.05 and a translational energy of under 1 eV. For multilayer films, these results show little, if any, dependence on the film thickness. This atom-based technique is envisaged as an alternative to ion sputtering for depth profiling of organic thin films. Since it involves only low-energy neutral species, charging effects are mitigated. Moreover, the incident neutral inert gas species does not react with the surface nor alter the chemical composition of the film.

*Sputtering of Ordered Ice  $I_h$  Adsorbed on Rh(111) Using Hyperthermal Neutral Ar Atoms*, K. D. Gibson and S. J. Sibener, *J. Phys. Chem. C*, **113**, 13325-13330 (2009).

The sputtering of ordered overlayers of water physisorbed on Rh(111) by hyperthermal Ar atoms was investigated. For incident kinetic energies of 10 to 20 eV, the impact of the Ar atoms leads to the desorption of intact single molecules. This sputtering is sensitive to the crystalline structure of the ice overlayers with the intensity and energy of the sputtered molecules being dependent upon both the final polar and azimuthal angles. The similarity between the results for 1 and 3 layers of water strongly suggests that all of the sputtering originates from the exposed topmost layer. In all cases sputtering yields are small,  $\sim 10^{-3}$ , and are inversely proportional to the film thickness; most of the energy transferred during the collision is dissipated into the lattice. These results suggest that sputtering of surfaces with hyperthermal neutrals might be useful as a non-charging and non-chemically-destructive adjunct to ion-induced sputtering and SIMS for compositional depth profiling and trace analysis. In this case only intact, neutral molecules are ejected, and the molecules left on the surface have not been altered.



*Atomic Scattering as a Probe of Polymer Surface and Thin Film Dynamics*, M. A. Freedman, A. W. Rosenbaum, and S. J. Sibener, *Phys. Rev. B*, 75, 113410/1-4 (2007).

Collisional energy transfer at the surface of poly(methyl methacrylate) thin films on SiO<sub>x</sub>/Si was investigated using low-energy neutral helium atom scattering. Analysis of spectra in two scattering regimes yields results consistent with the hypothesis that thinner films are stiffer, suggesting that for highly nanoconfined films, polymer-substrate interactions influence vibrational dynamics at the polymer-vacuum interface. Specifically, thinner films are found to have lower mean-square displacements and decreased annihilation events as compared to thicker films. The scattering spectra are fit well by a semiclassical scattering model, though deviations arise at sample temperatures near the bulk glass transition. We have found helium atom scattering to be a sensitive probe of the vibrational dynamics of the polymer thin-film surface. This technique holds promise for the exploration of glassy dynamics of polymer thin films.

*Polymer Surface and Thin Film Vibrational Dynamics of Poly(methyl methacrylate), Polybutadiene, and Polystyrene*, M. A. Freedman, J. S. Becker, A. W. Rosenbaum, and S. J. Sibener, *J. Chem. Phys.*, 129, 044906/1-9 (2008).

Inelastic helium atom scattering has been used to investigate the vibrational dynamics at the polymer-vacuum interface of poly(methyl methacrylate), polystyrene, and polybutadiene thin films on SiO<sub>x</sub>/Si(100). Experiments were performed for a large range of surface temperatures below and above the glass transition of these three polymers. The broad multiphonon feature that arises in the inelastic scattering spectra at surface temperatures between 175 K and 500 K is indicative of the excitation of a continuum of surface vibrational modes. Similarities exist in the lineshapes of the scattering spectra, indicating that helium atoms scatter from groups of similar mass on the surface of these polymer thin films. The lineshapes obtained were further analyzed using a semiclassical scattering model. This study has shown that quite different polymer thin films can have similar interfacial dynamics at the topmost molecular layer.

*Effects of Film Thickness and Molecular Weight on the Interfacial Dynamics of Atactic Poly(methyl methacrylate)*, M. A. Freedman, J. S. Becker, and S. J. Sibener, *J. Phys. Chem. B*, 112, 16090-16096 (2008).

We have investigated the surface vibrational dynamics at the polymer-vacuum interface of atactic poly(methyl methacrylate) thin films supported on SiO<sub>x</sub>/Si(100) as a function of film thickness and molecular weight. The highly surface-sensitive and non-destructive technique of inelastic helium atom scattering probes the vibrational dynamics at the true polymer-vacuum interface due to the lack of helium atom penetration into the film. For higher molecular weight samples (350 kg/mol), scattering spectra differ between films of thicknesses of fractions of the bulk radius of gyration compared with thicker films due to substrate interactions. A difference in the lineshape of the scattering spectra is also present for lower molecular weight samples (60 kg/mol) compared with the thick, higher molecular weight samples. The differences in scattering spectra indicate a reduction of interfacial surface vibrational motion for both the thin, high molecular weight and low molecular weight films as compared to thick, high molecular weight films. Our experiments demonstrate that dynamics at the interface of polymer thin films are unchanging until the films are thin enough for substrate interactions to influence vibrations at the true interface.

*Molecular Beam Induced Changes in Adsorption Behavior of NO on NiO(111)/Ni(111)*, B. D. Zion and S. J. Sibener, *J. Chem. Phys.*, 127 154720/1-6 (2007).

We have examined the adsorption behavior of NO on NiO(111) grown on Ni(111) at 110 K. High-resolution electron-energy-loss spectroscopy (HREELS) shows fundamental changes in the vibrational spectrum for the beam-dosed surface in comparison with the background dosed surface. Three vibrational peaks are observed after beam dosing, two of which are not observed

after conventional background dosing. The peaks can be assigned to NO stretches for a previously observed NO state, a new NO bonding geometry and a new NO<sub>2</sub> surface species, previously unobserved under NO dosing. The difference is accounted for by increased NO uptake due both to kinetically activated adsorption and to increased exposure.

*O-Atom Induced Gradual Deconstruction of the  $23 \times \sqrt{3}$  Au(111) Surface, K. D. Gibson and S. J. Sibener, J. Phys. Chem. A, 111, 12398-12401 (2007).*

He diffraction has been used to investigate changes in the surface morphology of reconstructed Au(111) when small quantities of O atoms are adsorbed. It is proposed that the electronegative oxygen removes charge from the surface, which causes the surface to revert to the (111) structure. The extent of this deconstruction is dependent on the initial O coverage and the surface temperature. These results further delineate and emphasize the delicate interplay of adsorbate coverage and surface structure for the oxygen – gold system, a topic of current high interest due to the remarkable and technologically relevant catalytic properties of gold interfaces and clusters spanning atomic through nanoscale dimensions.

*UV-Photodesorption of Novel Molecular Beam Induced NO Layers on NiO(111)/Ni(111), B. D. Zion and S. J. Sibener, J. Phys. Chem. C, 112, 5961-5965 (2008).*

The photodesorption and photoreactivity of the molecular beam dosed NO/NiO(111)/Ni(111) system has been examined using high-resolution electron-energy-loss spectroscopy (HREELS). The molecular beam-dosed surface exhibits three major vibrational peaks, which we attribute to a linear bonding NO species at 230 meV, a bent bonding NO species at 197 meV and a stretching mode of NO<sub>2</sub> at 160 meV. UV photon irradiation causes the attenuation of these peaks accompanied by simultaneous emergence of a fourth vibrational peak at 215 meV. The emergence of this peak is explained by a mechanism of selective desorption of the original, linear-bound NO species and a reaccommodation of the beam-induced, bent NO structure to a new state on the lower coverage surface. The measured desorption cross sections and wavelength dependence are consistent with other studies of photochemical processes on such interfaces, indicating that photo-induced electron transfer from the substrate to the adsorbate is the mechanism responsible for the observed behavior.

*Photochemical Study of the Transport Properties of Gases in Polymer Films, A. L. Cisse, E. Grossman, and S. J. Sibener, J. Phys. Chem. B, 112, 7166-7170 (2008).*

We describe a general method of finding the transport properties of molecules in polymer films by photolysis. PMMA samples held at different temperatures are exposed to UV radiation at discrete wavelengths and the time-evolution of the volatile photoproducts detected with a quadrupole mass spectrometer. A diffusion model is used to fit the experimental data and deduce diffusion coefficients for the main photoproduct methyl formate. The average value at room temperature was equal to  $1.9 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$  at all wavelengths investigated. Together with the values derived at other temperatures, an Arrhenius plot was obtained and the activation energy for methyl formate diffusion within the polymeric thin film calculated from the slope of the graph. We envision that this new method will find application to a variety of problems involving the mass transport of molecules through boundary layers of single or multilayer thin film structures.

*Hyperthermal Ar Atom Scattering from a C(0001) Surface, K. D. Gibson, S. J. Sibener (corresponding author), Hari P. Upadhyaya, Amy L. Brunsvold, Jianming Zhang, Timothy K. Minton, and Diego Troya, J. Chem. Phys. 128, 224708:1-7 (2008).*

Experiments and simulations on the scattering of hyperthermal Ar from a C(0001) surface have been conducted. Measurements of the energy and angular distributions of the scattered Ar flux were made over a range of incident angles, incident energies (2.8-14.1 eV), and surface

temperatures (150-700 K). In all cases, the scattering is concentrated in a narrow superspecular peak, with significant energy exchange with the surface. The simulations closely reproduce the experimental observations. Unlike recent experiments on hyperthermal Xe scattering from graphite [Watanabe et al., *Eur. Phys. J. D: Atomic, Molecular Optical Physics* **38**(1), 103 (2006)], the angular dependence of the energy loss is not approximated by the hard cubes model. The simulations are used to investigate why parallel momentum conservation describes Xe scattering, but not Ar scattering, from the surface of graphite. These studies extend our knowledge of gas-surface collisional energy transfer in the hyperthermal regime, and also demonstrate the importance of performing realistic numerical simulations for modeling such encounters.

## **VII. Concluding Remarks**

In this Final Technical Report we have discussed the scientific directions that we have pursued during the past grant period. This program uses a variety of perhaps unique scattering instruments complemented by *in situ* FTIR and XPS spectroscopy, SPM imaging, and commensurate theory/numerical simulations. The information generated on collisional energy transfer at complex and structurally controlled interfaces, thin molecular coatings, sputtering and erosion, and molecular transport/capture/release for these systems is relevant to the development of new high performance materials, while the training we have provided has helped educate the next generation of leaders in areas of direct interest to the AFOSR and DoD.

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